PHASE TRANSITION STUDIES OF SYSTEM OF THE TYPE $A_2Te_2X_6$

DISSERTATION

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CERTIFICATE

The work embodied in the dissertation entitled **PHASE TRANSITION STUDIES OF SYSTEM OF THE TYPE** $A_2Te_2X_6$ is original work carried out by Mr. SREEJITH.M.NAIR and is suitable for the consideration of the award of M.Phil. degree. This work was carried out under my supervision.

Afaq Ahmad

[Dr. AFAQ AHMAD]

DEDICATED

TO MY

GRANDMOTHER

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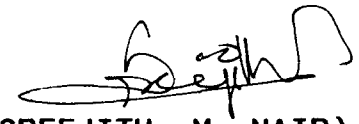

(SREEJITH. M. NAIR)

CONTENTS

CHAPTER 1

GENERAL INTRODUCTION

1.1 INTRODUCTION

Research in solid state chemistry is essentially concerned with investigation of structures and properties of solids, the primary motivation being understanding and predicting, if possible, the properties of solids in terms of their chemical compositions and crystal and electronic structures [1]. A crucial input in this enterprise is the synthesis of required material. From the early days, chemists have made significant contributions to the development of solid state sciences by synthesizing novel solids that possess unusual structures and properties [2]. Synthesis of unknown members in a structurally related family in order to extend and extrapolate structure - property relations and preparation of known compounds to investigate a specific property are the challenging and rewarding areas of solid state chemistry. Preparative effort in solid state chemistry become most rewarding when it is coupled with characterization and property evaluation [3]. This aspect of solid state synthesis is being increasingly recognized as illustrated by several articles [4-8] appeared in recent years.

The study of superionic solids is a new field of material science and technology. Most of the solid state devices developed in the last three decades are based on the

motion of electrons. Ionic solids have received very little attention in the past because of the nonavailability of solids with high ionic conductivity at room temperature. However, in 1967 the situation suddenly changed with the discovery of fast sodium - ion conduction in B-alumina [9] and silver ion conduction in $RbAg_4I_5$ [10]. Solids with exceptionally high ionic conductivity, in the range or .01 - 10 ohm^{-1} cm^{-1} , are termed as superionic conductors or fast-ion conductors or solid electrolytes. The class of the materials is extraordinarily diverse and includes simple inorganic compounds such as PbF_2 and AgI and organic polymers such as polyethylene oxide (PEO) doped with metal salts [11]. They have attracted considerable attention particularly during the last 20 years, owing to both their considerable potential in several technologies eg: solid state batteries, fuel cells, memory devices, display panels, atomic pumps etc. and the fundamental scientific interest in the phenomenon, high ionic mobility in solids. Even after so many years of discovery of superionic conductors, the research in this field continues to arouse the interest of the scientists the world over A complete understanding of the phenomenon, their particular features and the microscopic mechanism are not yet fully understand. An overview of the field can be obtained from the several conference proceedings [12-17] and reviews [18,19] that have been published in recent years.

1.2 SUPERIONIC CONDUCTING MATERIALS

The diversity of materials showing high ionic conductivity makes the classification difficult. The most important classes of superionic conducting solids are as follows

(a) Solids with phase transition

Some of the ionic conductors attain a high electrical conductivity only above a certain temperature. Those compounds for which the higher-temperature phase shows fast-ion behaviour are included in this class. The transition may be first order as in AgI or diffuse, Bredig transition, as in all fluorite structure materials [20]. The transition results in the generation of anion Frenkel disorder and it appears that both vacancies and interstitials are mobile in the superionic phase. More recently, the occurrence of Bredig transition has been clearly demonstrated in UO_2 [21].

(b) Layer and Tunnel structured compounds

For this compounds ion transport is confined to two or one dimensions, respectively. The β-Al_2O_3 in which the mobile cations are located in conduction planes between the spinel structured alumina block is a good example [22]. Despite the fact that β-Al_2O_3 is probably the most widely studied fast-ion conductor, knowledge of the basic migration mechanism is still uncertain. The stoichiometric material has

the composition $Na_2O_{11}Al_2O_3$ and has a structure, in which spinel structured alumina layers 'sand wich' conduction planes in which the mobile Na^+ ions are located, bridging oxygen ions are also present in these planes. The structure of β-Al_2O_3 is shown in Fig. 1.1. Wang et al. has proposed a widely accepted model of migration mechanism [23]. They suggested that excess Na^+ occupies a split interstitial configuration in which two Na^+ ions occupy mid-oxygen positions. Migration involves a saddle point in which the migrating ion occupies a normally vacant site. The calculations of Wang et al. gave activation energies for migration tnat agreed well with experiments. The widely studied NASICON compounds, which has the composition $Na_3Zr_2\ PSi_2\ O_{12}$ provides an example of a three dimensional tunnel structure [24].

(c) Heavily doped and massively disordered solids

Fluorite structured compounds can be doped, often to very high concentrations, with both low and high valence ions to creat high concentrations of mobile defects. Yttrium doped CeO_2 is a good example for low valence ions doping. Here the mobile defects are oxygen vacancies compensating the y^{3+} cation substitutionals [25]. The rare-earth doping of CaF_2 provides an example of the latter, the substitutional rare-earth atom now has excess positive charge and is

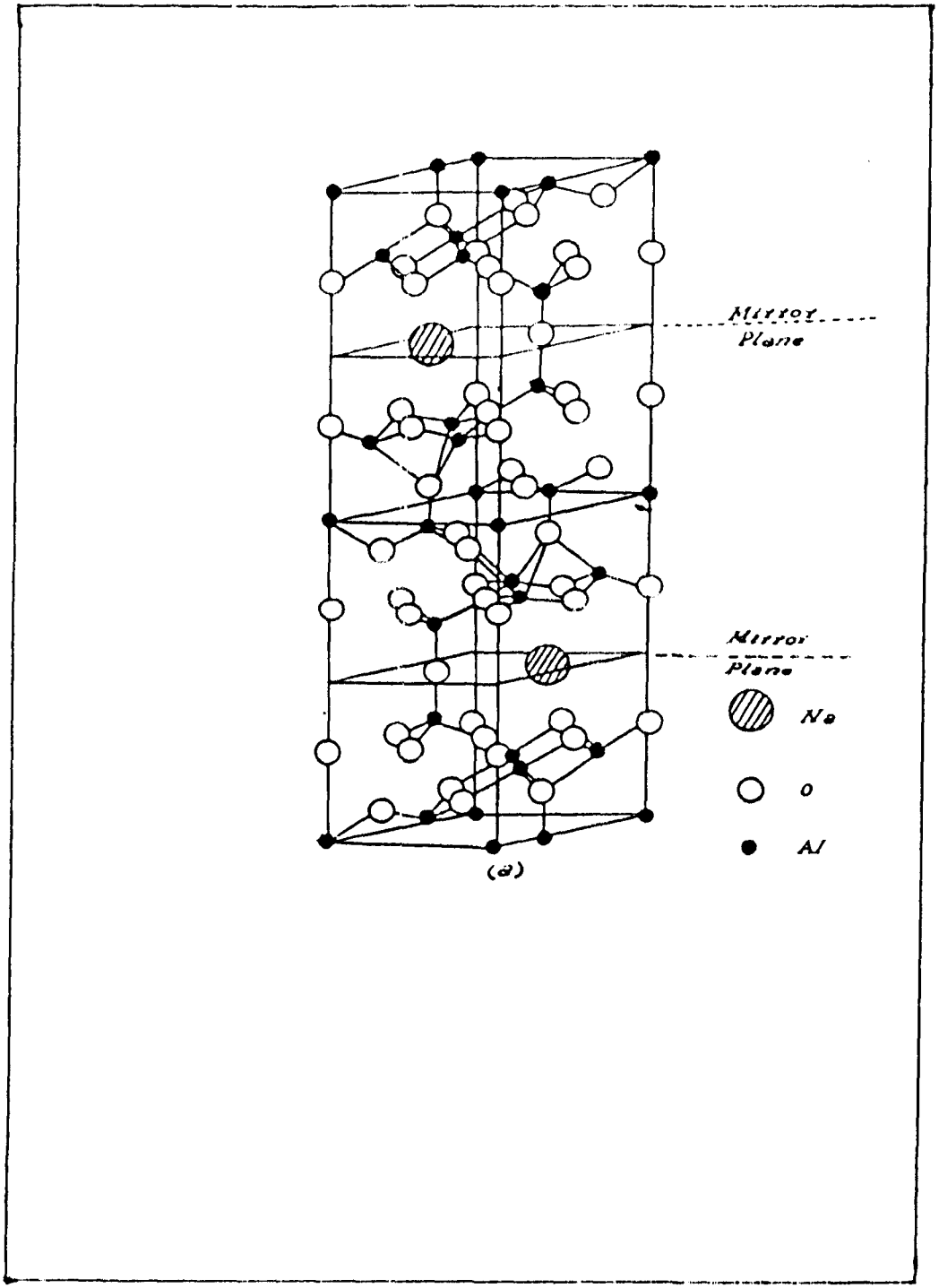

Fig. 1.1 Structure of β-alumina.

compensated by anion interstitials. Both anion vacancies and interstitials are mobile species in the fluorite structure [26]. But the low-valence doped materials have received greater attention as ionic conductors because of the higher mobility with vacancy activation energies being typically 0.5eV. The most important factor limiting the magnitude of the conductivity in this class of compounds is the nature of the dopent - defect interactions. For anion excess systems it has been extensively investigated and a fascinating range of cluster structure have been elucidated [27-29]. A subtly different example is provided by $RbBiF_4$, where the presence of the two types of cation results in the ready creation of anion Frenkel defects [30].

(d) Proton conductors

The materials with high proton mobilities are included in a separate class, owing to their distinctive transport mechanisms. Proton conductors can be usefully classified into hydrated materials and hydroxy containing oxides. Hydrogen uranyl phosphate ($HUO_2PO_4.4H_2O$) is one of the best example of the hydrated proton conductors [31]. The structure comprises layers of uranyl and phosphate ions separated by layers of hydrogen bonded water molecules. The structures of deuteriated samples of this materials have been studied in

details by Fitch and co-workers [32-34]. They found that the H_2O molecules are grouped into square planar arrangements held together by hydrogen bonding. Water molecules in different layers are also bridged by hydrogen bonds which reveal the presence of $H_5O_2^+$. The mechanisms proposed by Fitch et al. have been challenged with alternative models being proposed based on H_3O^+ migration and surface transport [35, 36].

One of the examples of the second class of proton conductors is provided by Yb doped $SrCeO_3$ [37], which has a distorted perovoskite structure. Yb dissolves into the lattice as cation substitutional with compensation by oxygen vacancies. Many perovoskite structured oxides can act as a proton conductors as appreciable oxygen vacancy concentrations can be introduced by doping.

(e) Amorphous and polymer-ion conductors

Current studies are increasingly focussing on non-crystalline ionic conductors which offer distinct advantages with regard to materials fabrication. Amorphous ionic conductors are not new materials. Ionic conductivity in silicate glasses has been extensively studied for several decades [38]. Recent work on conducting glasses has been concentrated on borate materials like $(Li_2O)_xB_2O_3$ which has high cation conductivity. In a review by Tuller [39] it has

been given a wide range of data on the variation of the conductivity with cation concentration and temperature.

Ionic conducting polymers are prepared by dissolving salts of monovalent ions into polyethers. Reasonable conductivity can be achieved and the materials have the major advantage in battery applications that they can readily be prepared as thin films [40]. The cations are solvated by the oxygen of the polyether and there is association between the solvated cations and the dissolved anions. The anions as well as cations are mobile in these materials, and the high mobility requires an amorphous polymer structure. The evidence of these mechanism has been obtained by EXAFS studies [41].

These classifications are not exhaustive. It includes, however, most of the materials that are currently the subject of active investigation.

1.3 MECHANISMS OF SUPERIONIC CONDUCTIVITY

There has been a substantial effort to understand the physics and chemistry of ionic compounds which have anomalously high ionic conductivity in the solid state [42, 43]. They are interesting from a fundamental point of view as a form of disordered solid whose properties, in certain respect, place them intermediate between normal solids and

liquid. Theoretical techniques, such as computational - lattice and defect simulations, molecular-dynamics and Monte-Carlo Methods [44], together with the major experimental investigations: ionic conductivity, specific heat, nmr, neutron scattering and light-scattering [45], have collectively led to our present understanding of the mechanisms of ion transport in these materials. Some of the different models suggested for the superionic conductivity will be discussed very briefly.

(a) Conventional transport mechanism

The transport is effected by a conventional hopping process usually of defects in a framework structured materials. There is no fundamental difference between the nature of these migration mechanisms in fast-ion and normal ionic conductors, but the defect may be present in exceptionally high concentrations and may have very low activation energies. A good example is provided by CeO_2 doped with y^{3+} [25]. The conductivity is based on the rapid transport of vacancies, which are, however, migrating by a conventional hopping mechanism. The defect chemistry of these materials is based on the replacement by trivalent ions of the host cations with compensation by oxygen vacancies; the latter have activation energies of about 0.5eV and they may be

present in high concentrations in the fluorite host owing to the high solubility of low valence substitutionals. The material shows intriguing variations of the conductivity with the dopant concentration. Gerhardt - Anderson and Nowick et al. show that for dopant concentrations of less than 1 mol% oxygen, transport can be analysed in terms of the equilibrium between clusters and free valencies [46].

Thus to summarise, oxygen transport in these materials takes place by conventional vacancy hopping process. At low concentrations, dopant-defect interactions may be described by the formation of simple pair clusters, while at higher concentrations it is better to think of the problem using percolation models.

(b) Correlated migration mechanism

In this category the rapid ion transport is effected by several ions moving together in a concerted manner. Simulation methods are having great value in revealing the details of such mechanisms. Li_3N and Rb BiF_4 are good examples to explain this mechanism.

Li_3N is possibly the best known Li^+ ion conductor with an appreciable conductivity of 10^{-3} ohm^{-1} cm^{-1} at 50^oC [47]. The crystal structure comprises Li_2N layers containing hexagonal arrays of Li ions which are linked by bridging Li^+

ions which lie between N^{3-} ions in adjacent layers. The structure of Li_3N is shown in Fig 1.2. The molecular dynamics simulation techniques [48, 49] applied to Li_3N produce the following important mechanistic informations; (i) Li^+ ions can be readily excited thermally from the Li_2N layers into the gaps between the layers. (ii) The vacancies that are thereby created can migrate rapidly through the crystal by highly correlated mechanisms. This high degree of correlation in the Li^+ ion motion is a key factor in promoting a high conductivity.

The high conductivity of $RbBiF_4$, the cation disordered fluorite structured material, was first shown by Reau and co-workers [50,51]. The material has the fluorite structure with disordered distribution of Rb and Bi over the cation sites. The EXAFs studies shown that disorder is generated preferentially around the Rb ions. The interstitials in the fluorite structure migrate by the interstitialcy mechanism in which the migrating F^- ion displaces neighbouring lattice ions into interstitial sites. The ions are again moving in a correlated manner, the motion of each ion being of the interstitialcy type. As with Li_3N, ease of creation of the defects is vital for the high conductivity; but correlated migration mechanisms are again clearly of central importance.

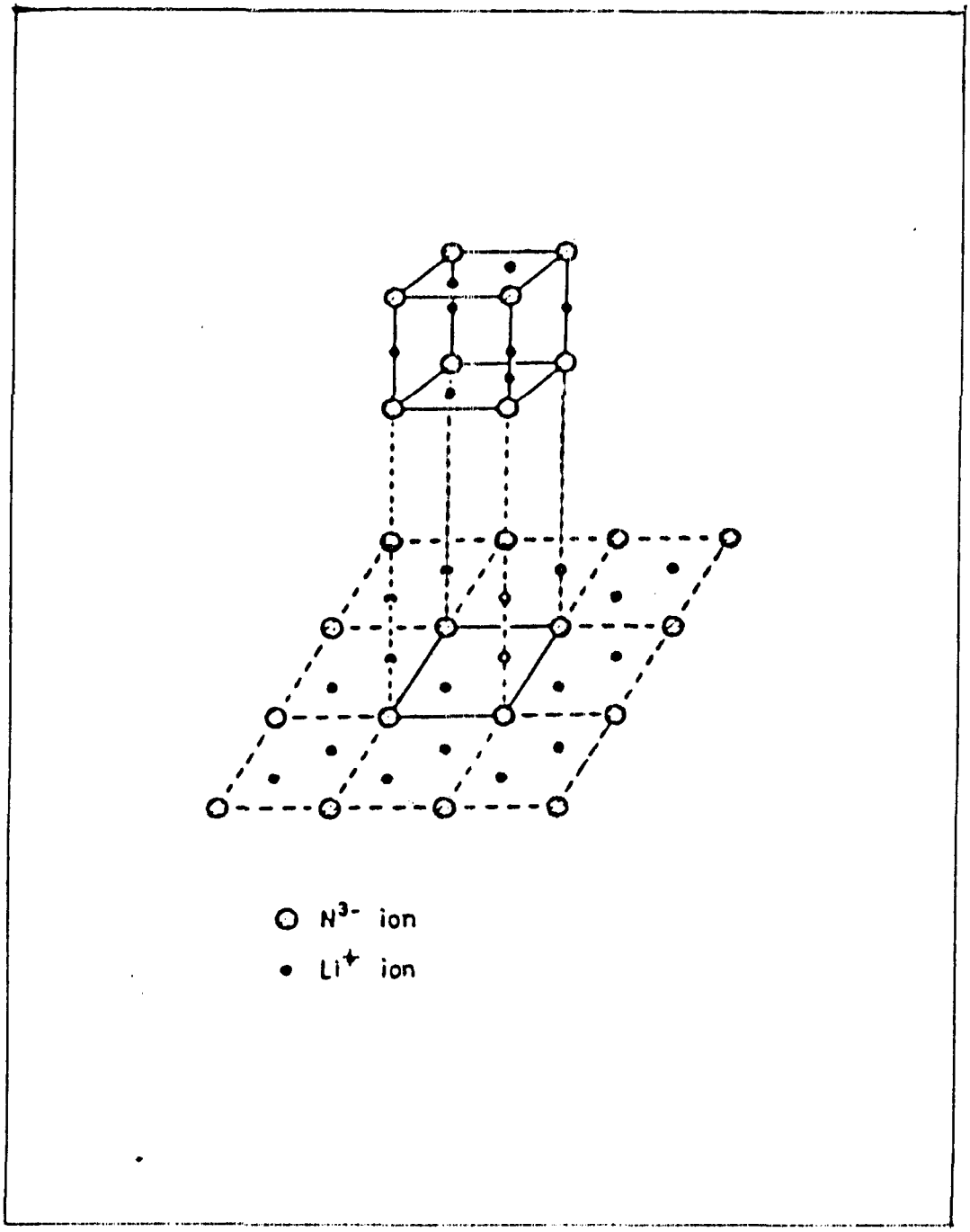

Fig. 1.2 Structure of Li_3N.

(c) Liquid-like diffusion mechanism

Here the mobile sublattice is highly disordered and which transport cannot be interpreted in terms of hopping between distinct lattice sites. There are very few materials for which this is an accurate model for the ion-transport mechanism. There is,however, good structural evidence for very high degree of cation disorder in certain silver chalcogenides like Ag_2S [52] at high temperatures. It seems therefore that in these materials the cation sublattice is structurally liquid like, it is plausible therefore to suggest that the transport mechanisms have a similar character.

(d) Intermediate mechanisms

Here it includes materials where the lattice-hopping models are breaking down and those for which there is a transition from hopping to liquid-like transport. A good example of the first case is provided by AgI which undergoes a phase transition at $147^{O}C$ from wurzite structure to a structure based on a bcc I^- sublattice with a disordered distribution of Ag^+ over the tetrahedral sites, the high temperature phase shows high Ag^+ ion mobility [53]. Neutron diffraction and quasi-elastic neutron scattering studies of Wuensch and co-workers have clearly demonstrated the

localization of the silver ions in the tetrahedral sites of the superionic conducting phase [54-56].

Second example is the interesting material Li_2MgCl_4 which has an inverse spinel structure in which Li^+ ions are distributed between octahedral and tetrahedral sites [57-59]. NMR and conductivity studies suggest a change in the ion transport mechanism in temperature range 500-700 K, which is manifested by a 'knee' in the conductivity versus 1/T plot. At low temperatures the lithium transport mainly involves the octahedral lithium ions which migrate by a hopping mechanism between the octahedral sites, via a tetrahedral site. At higher temperatures the mobility of the lithium ions on the tetrahedral sites becomes appreciable and a large fraction of the ions are found to via non-hopping mechanisms [60].

1.4 PHASE TRANSITIONS IN SUPERIONIC SOLIDS

The high ionic conductivity achieved by most of the superionic conductors is via well defined phase transitions at a particular temperature. With increasing temperature the electrical conductivity sometimes changes gradually as in β-alumina [9] or shows an abrupt jump as in β-AgI, $RbAg_4I_5$ etc. [10].

Pardee and Mahan [61] categorised the phase transition into two. First kind is called Insulator - electrolyte phase

transition in which there is an abrupt jump in the conductivity versus 1/T curve. The transition is sometimes associated with a distinct structural change and the latent heat change is typical of a first order transition. The second kind is called order-disorder phase transition in which there is no abrupt change in conductivity, the conductivity versus 1/T plot is continuous with a small change in slope at the transition temperature. The specific heat will change gradually with temperature and generally no change in lattice symmetry. The electrical conductivity of a few superionic solids undergoing the above types of phase transition are collected in Fig. 1.3. The abrupt increase in conductivity is observed for a few cases characteristic of insulator-electrolyte phase transitions. The transitions at 151°C for $RbAg_4I_5$, 147°C for AgI, 890°C for LuF_3 are of first kind. The phase transitions at T = 64°C for $RbAg_4I_5$, 50°C for silver pyridinium iodide, 190° for $(CeF_3)_{0.95}(CaF_2)_{0.05}$, 1150°C for CaF_2 represent typical order-disorder transition.

(a) Phenomenological theories on phase transition

For the transitions of first kind the phase theory of Gibbs provides a satisfactory thermodynamic net work that can be supplemented by more specific information derived

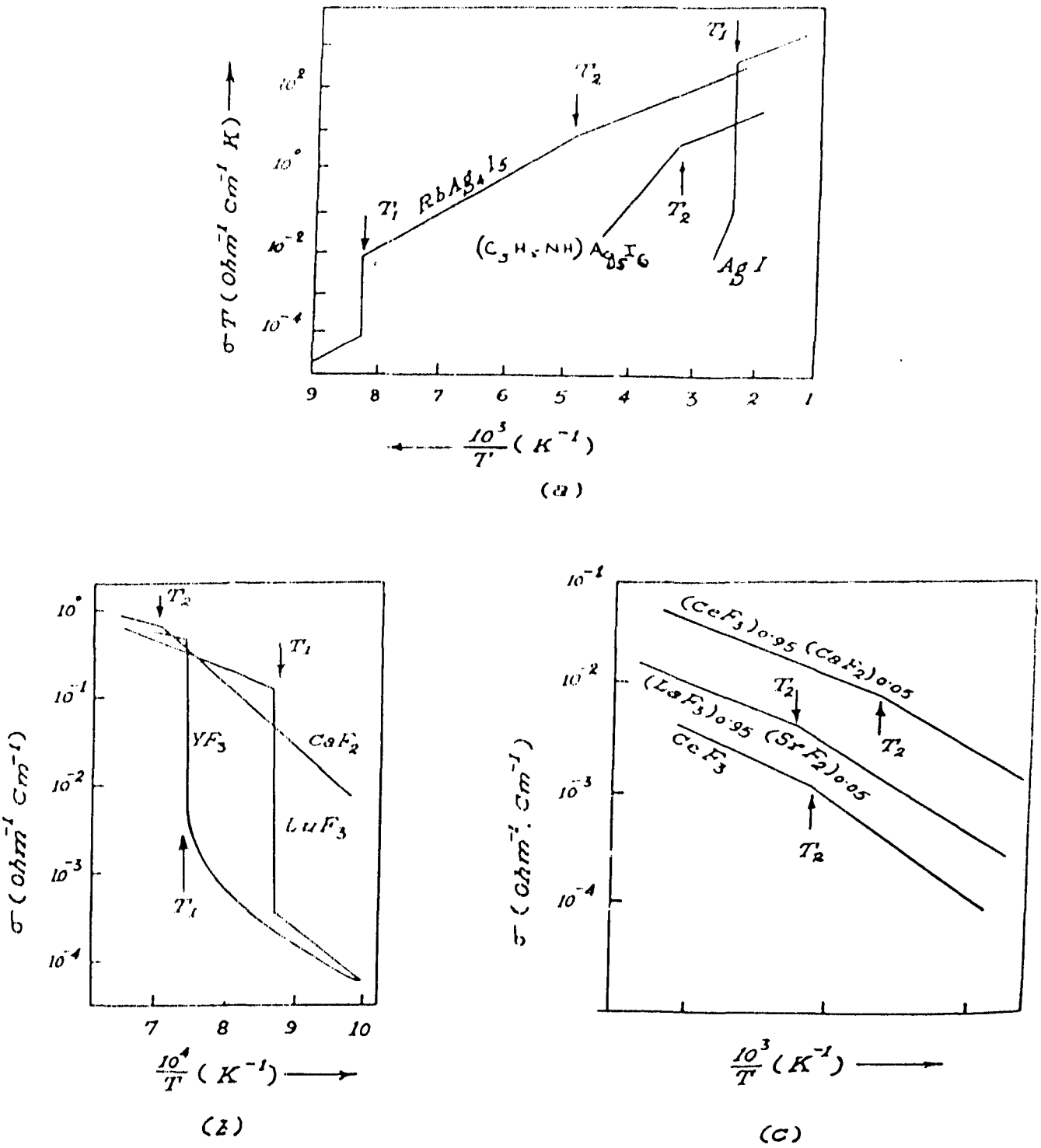

Fig. 1.3 Ionic conductivity of some superionic solids showing Class-I and Class-II types of phase transition.

primarily from experiments. The X-ray and neutron diffraction methods supply detailed information about the geometry of the lattice. Measurements of rates of transitions give some information about the free energy barriers separating the different polymorphic modification.

The essential thermodynamic features of the second kind have proved more elusive. In fact transitions of the second kind mark the onset of ferromagnetism, ferroelectricity and superconductivity and establishment of various types of molecular order in alloys and in the molecular crystals [62].

The high conductivity is generally sustained by materials showing a high degree of disorder, permitting many ion jumps to take place simultaneously. The thermally generated defects are made to interact in such a manner that the charge carrier density increases either abruptly or discontinuously resulting in an abrupt increase in conductivity. Hubermann [63] showed that a Frenkel pair attractive interaction is responsible for the superionic phase transition. The crystals always contain a finite number of Schottky and Frenkel defects, which increases with temperature. He considered the case of formation of Frenkel pairs by ions leaving their normal sites and going to available interstitial sites. The conductivity depends on the number of Frenkel pairs, which is an exponential function of

the activation energy for their formation. The total activation energy is rendered defect - concentration - dependent by assuming that there is an attractive interaction between the interstitial ion and the vacancy, proportional to the square of defect concentration.

Almost simultaneously Rice et al. [64] gave a model for the transition to the superionic state which they showed was due to the interatitial defects interacting with the strain field they induced. According to them the creation of interstitials will lead to a finite change in the volume of the crystal putting the solid in a state of hydrostatic strain. The free energy is assumed to be a function of defect concentration and strain. They proposed a ratio λ/U_i where U_i is the energy required to promote a cation to an interstitial site and λ is an interaction parameter given by $\lambda = r^2/W_o$ which inturn is related to the bulk modulus and the number of cations per unit volume. For a small value of λ/U_i (=0.1) the number of defects increases smoothly with temperature and hence the σ versus 1/T plot would be the same as for the normal ionic solids. For λ/U_i approximately equal to but less than 0.97 the rate of increase of defect concentration changes at a certain temperature and the slope of the curve changes without an abrupt change in conductivity. But for $\lambda/Ui > 0.98$, the defect concentration

rises abruptly and hence it corresponds to the case of first order transition normally occuring in superionic solids. Welch and Diene [65, 66] have suggested in a more general way two models by which the thermally generated defects concentration modifies the free energy of the ionic crystal such that different orders of phase transition result.

(b) Lattice gas theories of phase transition

In earlier theories, the first and second kind superionic transitions and σ versus 1/T behaviour were explained on the basis of the change in the number of charge carriers due to ion interactions. If we have a large number of charge carriers as a result of first-order phase transition, the mobile ions can be considered as a 'lattice gas' hopping from one lattice point to another. These particles interact with each other and can modify the ion diffusion or transport activation energy [67]. Explaining the migration here it is used the path probability method. The earlier random walk approach failed because it requires the jump frequency of an atom to an adjacent site to be constant, independent of location and time. But in the case of fast-ion conductors with highly disordered lattice, the number of vacancies are comparable with that of migrating cations and

hence jump frequency of ions will be influenced greatly by their immediate surroundings.

In another theory proposed by Mahan [68], the solid is represented as a network of sites at which the ions can sit. The number of available sites is greater than the number of ions. It is assumed that there is a repulsive interaction between nearest neighbours. An ion polarizes the host crystal, and hopping must carry this polarizing cloud with it. The presence of appreciable disorder below the transition temperature (T_c) is a manifestation of the slow rise of the order parameter with decreasing temperature. That is, both above and below the transition temperature there is substantial disorder, even though this temperature corresponds to an order-disorder transition suggested by Pardee and Mahan. From the structural studies Geller [69] has also identified this transition as a disorder-disorder transition.

1.5 ELECTRICAL CONDUCTIVITY OF IONIC SOLIDS

Electrical conductivity measurements were amongst the earliest physicochemical measurement that were made on solids. All ionic material have an electrical conductivity in the solid state due to the diffusive motion of the ions. In most such materials, this diffusion is associated with the

motion of point defects created either by thermal excitation or by doping. The concentration of thermally generated defects in most ionic materials is extremely low. But in superionic conductors the thermal disorder is too large at high temperature that the conductivity attains liquid-like values [70-74].

Tubandt and co-workers were the first to verify the Faraday's law of electrolysis in ionic solids [75]. It is a modification of Hittorf's experiment used to determine transport numbers of electrolyte solution. Their experiments allowed transport numbers to be evaluated and revealed a wide range of behaviour. The diffusion process can be expressed analytically by Fick's law which states that the number of atoms crossing a unit area per unit time, J, is proportional to the gradient of their concentration N,

$$J = - D \frac{dN}{dt}$$

where D is the diffusion coefficient.

The diffusion is materialized in four different ways. Direct interchange between two atoms, migration of an interstitial atom, atomic displacement into a neighbouring vacancy and diffusion of pairs of vacancies are that distinct process [76]. The sum of the energies of defect formation and

subsequent migration is called the activation energy of that process. The temperature dependence of the coefficient of diffusion is related to the activation energy E by

$$D = D_o \, e^{-E/kT} \qquad \ldots\ldots (1)$$

where D_o is a constant for a crystal

The ionic conductivity due to monovalent ions of one sign is given by

$$\sigma_{ionic} = e N \mu_{ionic} \qquad \ldots\ldots (2)$$

where N is the number of ionic sites of one sign and μ is the mobility of ions.

According to Einstein, the mobility of these ions is

$$\mu_{ionic} = \frac{eD}{kT} \qquad \ldots\ldots (3)$$

Combining equations 2 and 3 and substituting equation 1 for D, the ionic conductivity is given by

$$\sigma_{ionic} = \frac{e^2 N}{kT} D$$

$$= \frac{e^2 N}{KT} D_o \, e^{-E/kT} \qquad \ldots\ldots (4)$$

Data analysis:

The simplest first step in the analysis of the conductivity data is to determine the Arrhenius energies from the plot of log σ versus 1/T. The slope of the curve gives directly the value of activation energy E. The next stage is to attempt to relate these to the microscopic conduction process.

The specific conductance of a substance is given by the relationship

$$\sigma = \sum_{r=1}^{i} n_r / q_r / \mu_r$$

where n_r is the number of conducting species of type r per unit volume, q_r and μ_r are charge and mobility respectively. The value of n_r can be written down in terms of point defect equilibria. If the predominant point defects are Schottky pairs, that is, a cation vacancy 'CV' and an anion vacancy 'av' the defect equilibrium can be described by the quasi-chemical expression.

$$O = CV + aV,$$

where 'O' is the perfect lattice. A cation and an anion vacancy can form a neutral vacancy pair 'VP' and cation

vacancy can form a neutral complex 'CP' by association with a divalent cation impurity M^{2+}. This can be described by the quasi-chemical expressions

$$CV + aV = Vp$$
$$M^{2+} + CV = CP$$

respectively.

The law of mass action can be applied to each expressions to yield the equilibrium constant in terms of the defect concentrations. It is possible to solve the mass action equations using the constrains of charge and site balance and to write down an explicit expression for the concentration of any defect in terms of the thermodynamic parameters governing its formation and association with other defects [77].

Beaumount and Jacobs [78] suggested a computer least-square fitting method for conductivity data analysis. This method has been used to determine the defect parameters in a wide range of simple ionic solids, including the alkali halides [79-81] AgCl and AgBr [82] and the fluorite structured halides [83]. The quality of the conductivity data and the fitting can be judged from the works on silver halides. Conductivity studies have proved to be rather

complex in these systems. The intrinsic disorder is cation - Frenkel pairs and the interstitial Ag^{+} ions can diffuse via two mechanism: the collinear and non-collinear interstitialcy mechanisms. This increases the number of adjustable parameters in the fitting to 11 compared with 9 used in the simplest model to analyse the conductivity of the alkali halide crystal.

Conductivity measurements are the best method, of obtaining accurate defect parameters in strongly ionic materials and studying the phase transition in these materials. In near future the conductivity measurements and calculations on more complex systems will be very fruitful.

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CHAPTER 2

ELECTRICAL CONDUCTIVITY AND PHASE TRANSITION STUDIES ON PURE AND DOPED Ag_2HgI_4 AND Cu_2HgI_4 SYSTEM

2.1 INTRODUCTION

The importance of solid solution or mixed crystals over individual crystal is that their properties such as conductivity, reflectivity, dielectric constant etc. are different from the individual compounds and have found wide applications in industry.

The present trend in searching for superionic conductors for battery material and other devices is two-fold in nature [1-4].(i) to find new materials showing high values of ionic conductivity in the vicinity of room temperature, and (ii) to use known ionic conductors with other materials in the form of mixed systems to increase the conduction efficiency. The latter procedure attracted considerable attention in recent years as it not only lowers the superionic phase transition temperature but also gives relatively high values of conductivity. One of the best kind of such systems is $RbAg_4I_5$, which is a mixed salt of RbI and AgI [5,6]. This mixed system shows very high ionic conductivity even below room temperature.

Ag_2HgI_4 is a well known superionic conducting material first studied by Ketelaar [7]. Since the observation in the 1930's of a phase transition at 50^oC in Ag_2HgI_4, many investigations have been reported on the electrical

conductivity [8,9], thermo electric power [10], heat capacity, X-ray diffraction [11] and Raman scattering [12] of this solid electrolyte.

Neubert et al. observed a decrease in electrical conductivity of Ag_2HgI_4 in the β-modification upon cycling to T > 50°C, and suggested this is due to the growth of crystallites and increasing perfection of crystallites. Further cursory examination of β-modification, conductivities as a function of pressing pressure and pressing time show that the σ -values were greater the higher the pressure and the longer the time samples are held at top pressure. The annealing and pressing behaviour together with a study of dielectric properties, suggested that the bulk of the specimen consist of relatively large grains of ordered crystals. The grains contacted one another via point contacts of poorly organized boundary material. Where the grains were not in contact there were non-conducting voids. Contact materials, because of its high state of disorganization, and therefore low degree of order, are presumed to have a high conductivity. Transformation of disordered materials into ordered material by grain growth during annealing together with a concomitant decrease in the number of contacts causes specimen conductivity to decrease.

The frequency dependence of the conductivity of Ag_2HgI_4 observed by Shibata et al. [13] is similar to that found for CuCl [14] pellets and AgBr [15] crystals. The results were interpreted in terms of equivalent circuits composed of resistance and capacity contribution at the sample electrode interface. They were attempted to determine the transport number of the electronic component in Ag_2HgI_4 and the results indicate that for the β-phase the conductivity could have a smaller electronic contribution; 1-10% of the total conductivity. The values of electronic conductivity are much smaller than those reported by Weil and Lawson [16] and Webb [17], suggesting the Ag^+ ion is still the dominent charge carrier in the β-phase Ag_2HgI_4 and the conductivity behaviour of the β-phase is strongly sensitive to the sample preparation.

α-Ag_2HgI_4 is often classified as one of the superionic conductors with exceptionally high ionic conductivity [18]. However, the activation energy for ionic motion for α-phase are much larger than those of other superionic conductors such as AgI or β-Al_2O_3. It has been suggested that this was due to the fcc arrangement of the I^- sublattice so that the Ag^+ ion was forced to go through the high energy octahedral interstices in the transport process [5]. Therefore the free-ion model proposed by Rice et al.

[18] is inappropriate because of the mean free path fitted to the conductivity data is too long to be accepted. Atomic transport processes in α Ag_2HgI_4 may be interpreted in terms of the usual interstitial - jump mechanism.

The microwave complex conductivity of Ag_2HgI_4 [19] indicated hopping is the basic transport mechanism in the ionic conducting α-phase. Activation energy for microwave conductivity were all found to be lower than that of the dc conductivity. These observations were in support of the earlier suggestion attributing the high dc activation energy and prefactor to high potential barriers the Ag^+ ion must overcome in a long range transport so that hopping rather than free particle theory is appropriate.

It was Ketelaar who noticed first, the ionic conductivity of Cu_2HgI_4 [7,20]. It has been reported that Cu_2HgI_4 exhibited ionic conductivity and it showed a phase transition from the low temperature phase with ordered tetragonal structure to the high temperature phase with disordered pseudocubic structure [8,21]. Studies conducted by Shibata et al. [13] showed the values of the conductivity were dependent on the applied frequency, but were nearly constant in the low frequency region for the β-phase and high frequency region for the α-phase. For β-Cu_2HgI_4 the electronic conductivity is almost equal to the total

conductivity. But above 76^{O}C at ambient pressure Cu_2HgI_4 transforms from an ordered electronic conductor into the α - phase which displaces mixed ionic and electronic conductivity.

From the far infrared transmission and reflection measurements [22] on Cu_2HgI_4 in both α and β phases showed that the mobile ions Cu^+ have a solid-like motion compared to the liquid-like motion in α-AgI. Hence the mobile motion can be described by damped simple harmonic oscillators. The mobile ions move from one tetrahedral site to another equivalent tetrahedral site and they occupy an interstitial octahedral site during their conduction process. This sort of conduction mechanism is in good accord with the Wiedersich and Geller [5] model for these materials.

Thus it appears that, even though a good understanding of the mechanism of ionic transport in pure Ag_2HgI_4 and Cu_2HgI_4 has been achieved, the behaviour of these compounds with guest ions in their lattice is not yet clear. Therefore we planed to undertake a detailed investigation in the doped Ag_2HgI_4 and Cu_2HgI_4. The study in the doped system is motivated by the fact that many other systems like Ag_2SO_4 [23] have shown higher conductivity on doping with lighter ions. The phase transition temperature in some compounds have

been found to change with the dopant size and dopant concentration. In the present study, we have chosen Cd^{2+}, K^{+} and Na^{+} as the guest ions.

2.2 CRYSTAL STRUCTURE

Structure of Ag_2HgI_4 and Cu_2HgI_4 based on X-ray powder diffraction pattern were proposed by Ketelaar [24] and Hahn [21]. Later Kasper and Browell employed single crystal X-ray crystallography to obtain refined structures for the alpha (disordered) [25] and beta (ordered) [26] phases of Ag_2HgI_4. The structure of high temperature α -phase and low temperature β-phases of Ag_2HgI_4 and Cu_2HgI_4 are shown in Fig. 2.1. In the β-phases the iodides form a face-centered cubic lattice with the two silver or copper ions and one mercury ion occupying three of the four available tetrahedral sites, leaving one quarter of the tetrahedral sites empty. The two salts differ in the relative position of the cations and the empty sites. The primitive Wigner-Seitz cell of the copper compound shows higher symmetry (D_{2d}) than that of the silver salt (S_4). The lattice parameters of Ag_2HgI_4 are $a=6.3A^{o}$ and $C=12.6A^{o}$ at room temperature. But above $52^{o}C$, Ag_2HgI_4 transforms from the yellow β-phase to the brick-red α -phase with the three cations randomly distributed among the four tetrahedral sites provided by the fcc sublattice of the I^{-} ion. Above the phase transition, in the Cu_2HgI_4, the

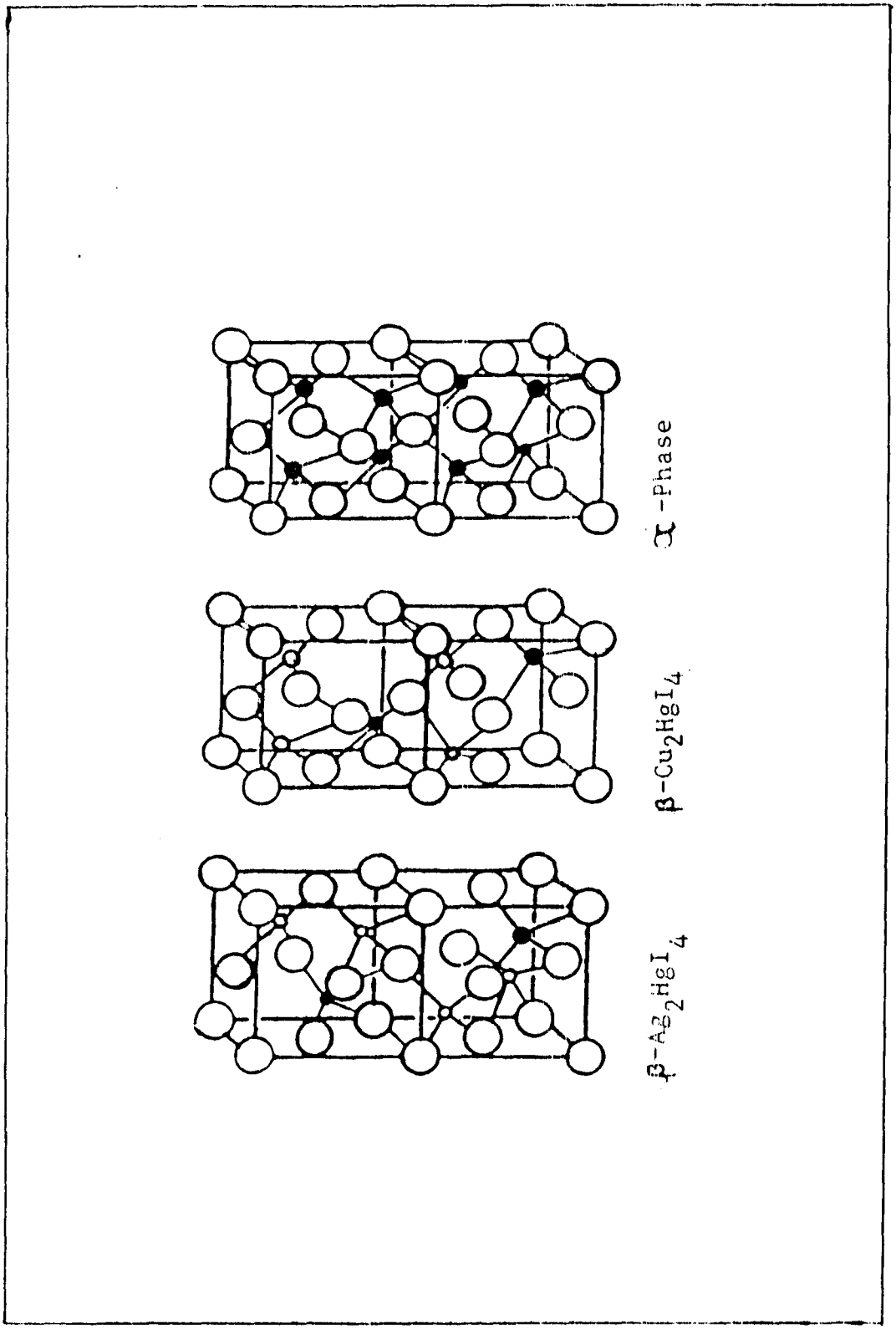

Fig. 2.1 Structure of the β-phases and α-phase of Ag_2HgI_4 and Cu_2HgI_4.

cations disorder to partially occupy all of the tetrahedral sites and the two compounds become isostructural.

2.3 EXPERIMENTAL DETAILS

(a) Preparation of Ag_2HgI_4

Although Ag_2HgI_4 is known to be formed in solid state by the interaction of AgI and HgI_2, this method was not followed for its preparation. It was prepared by simultaneous precipitation from solution containing stoichiometric amounts of reactants. This method yielded more satisfactory results than solid state product. Ag_2HgI_4 was precipitated slowly, and with vigorous stirring, from 0.5M K_2HgI_4 solution by addition of the stoichiometric amount of 1M $AgNO_3$ solution [28]. Analar Grade chemicals (KI, HgI_2 and $AgNO_3$) were used. The precipitated powder was washed 10-15 times by decantation, filtered and dried over P_2O_5. The preparation was carried out in diffuse light using brown bottles, but otherwise no extraordinary precautions were taken to avoid photochemical effects. X-ray diffraction studies showed typical diffraction pattern of the Ag_2HgI_4, and the d values match well with the ASTM powder diffraction file.

(b) Preparation of Cu_2HgI_4

Cu_2HgI_4 was prepared by simultaneous precipitation from solutions containing stoichiometric amounts of

reactants. Aqueous solutions containing mixtures of $CuNO_3$ (BDH, Analar Grade) with total metal ion concentration about 0.4M was added to boiling solution of approximately 0.1M K_2HgI_4 which was earlier prepared by mixing stoichiometric solutions of $Hg(NO_3)_2$ and KI in sufficient quantity to remove the iodine formed [29] and to decrease the loss of material remaining in solution. If this was not done, results were found to be poor, the product consisting largely of CuI rather than Cu_2HgI_4.

Cu_2HgI_4 obtained as dark red mass was filtered and washed with KI solution and double distilled water, dried thereby over porous plate in a thermostat at about 100°C X-ray diffraction studies showed it to be low temperature single phase ß-Cu_2HgI_4. The calculated d values matched well with the ASTM powder diffraction file [30] and the intensities also matched well.

The doped compounds (Cd^{2+}, K^+, Na^+) were prepared by heating at 200°C for 24 hrs the requisite dopant composition, previously ground manually in a mortar, of the respective iodomercurates in a silica crucible.

(c) Conductivity measurement

In order to measure specific conductivity as a function of temperature, the sample powders were pressed into pellets

of 2.5 cm diameter and .1 cm thickness at a pressure of about 2 tons [31], with the help of Spectra Lab press (Model SL-89). Pellets were found to be of the same colours as the original powders. However, higher pressures were found to cause uneven darkening in the pellets and lead to higher transition temperatures. Before making measurements, samples were cycled to above and below the transition temperature two or three times in order to relieve strains and improve their homogeneity.

It was then placed between two discs of platinum foil. Adequate electrical contact between the platinum and the pellets was ensured by placing the pellets and the platinum discs between two copper plates, to which leads were attached, held tightly together by placing a fixed weight. This assembly was then placed inside a thermostat . The temperature was brought to each desired level and kept there for about 15 minutes to ensure that equilibrium had been reached. A Gen Rad 1659 RLC Digi Bridge with the frequency range 100 Hz - 10 kHz was employed for measuring conductivity. Possible impedence contribution from external connection cables and pellet mounting devices were corrected by using its built in 'short' and 'open' calibration facility. Determinations of conductivity were made over the range 25 to 200^{O}C. Possible volume expansion of the pellets

was not monitored and the thickness measurements of the pellets were performed after the sintering.

2.4. RESULTS AND DISCUSSIONS

(a) Electrical conductivity studies of Ag_2HgI_4 - Cu_2HgI_4 Solid Solutions

The curves for the specific conductivity as a function of increasing temperature for pure Ag_2HgI_4, 50:50 mol% Ag_2HgI_4: Cu_2HgI_4, 33:67 mol% Ag_2HgI_4: Cu_2HgI_4, 67:33 mol% Ag_2HgI_4: Cu_2HgI_4 along with pure Cu_2HgI_4 are presented in Fig. 2.2 The usual log (σ T) versus 1/T system of coordinates were used to present the data. The conductivity values found for Ag_2HgI_4 were very near to those reported by the earlier workers [8,9] conductivity values show a remarkable change at 52°C, the phase transition temperature of Ag_2HgI_4. The conductivity plot for Cu_2HgI_4 shows a change in slope at the transition temperature (67°C) which indicate an increase in ionic conductivity at that point. However, the activation energy for the β-phase is lower than that of the α-phase. The lower activation energy value is due to the presence of electronic conductivity which would contribute a higher percentage of the current to the β-phase than to the α-phase.

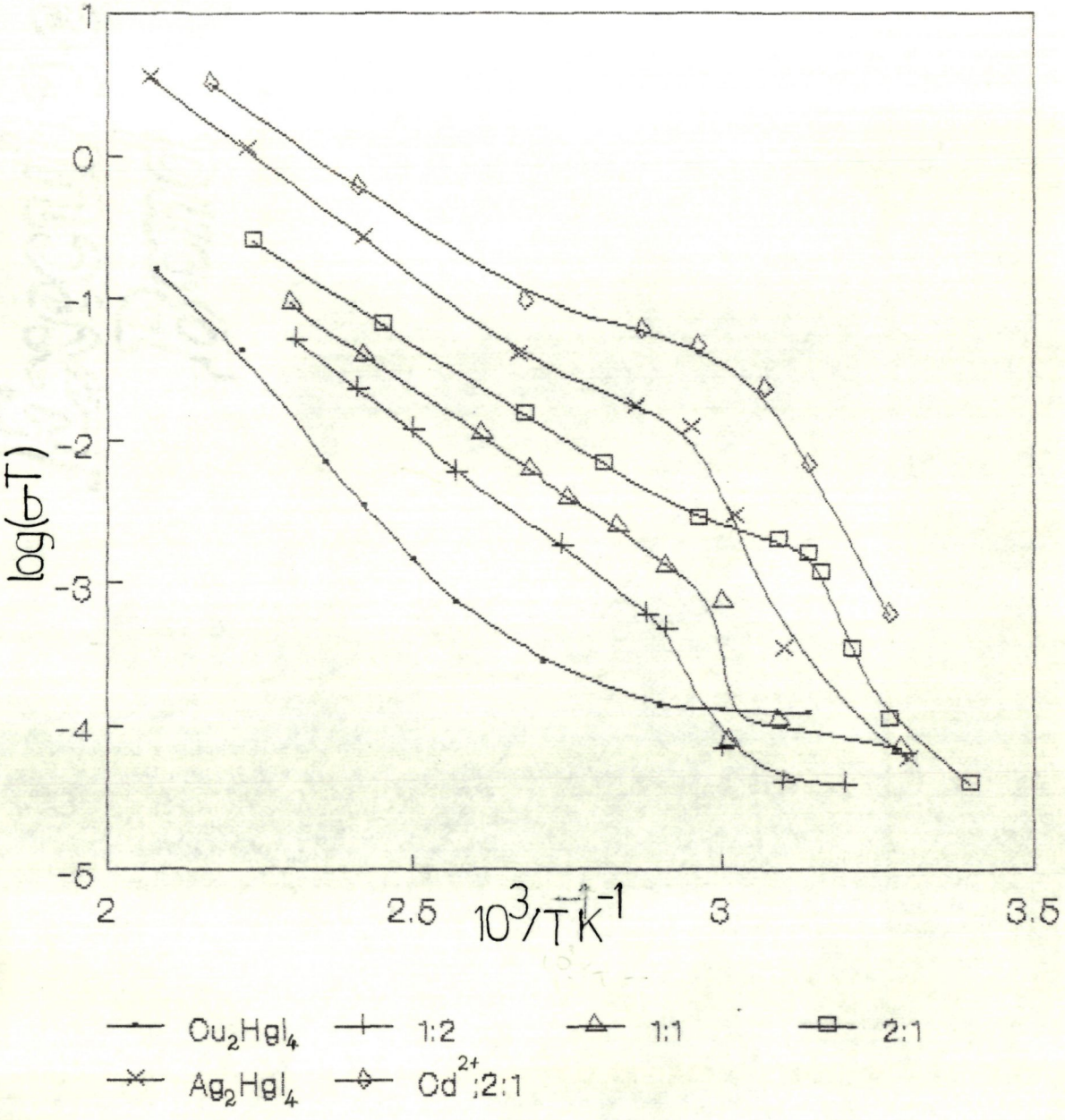

Fig.2.2: Temperature dependence of the electrical conductivity of pure and doped Ag_2HgI_4-Cu_2HgI_4 systems.

The frequency dependence of conductivity of Cu_2HgI_4 is shown in Fig: 2.3. Conductivities of ß-phase increases with frequency so that inferences to their transport mechanism must be made together with consideration of their temperature dependence. As the temperature increases the variation in conductivity becomes less and above the phase transition, conductivity is almost independent of frequency.

From Fig.2.2 it may be seen that the conductivity values for the solid solutions are intermediate between those for the parent compounds, and that all exhibit sharp rises in conductivity at characteristic transition points after preliminary increase starting several degrees lower. The curves as plotted are not to be considered absolute, but rather average values, since somewhat varying results were obtained depending upon the history of the sample and the pellet. Such factors a pressure and heat treatment were especially found to affect the levels of the curves both above and below the transition points, but their slopes were not affected.

The phase transition temperatures of the pure and various solid solutions of Ag_2HgI_4 and Cu_2HgI_4 are given in table 2.1 .The transition temperatures of the solid solutions are also intermediate between those of the parent compounds,

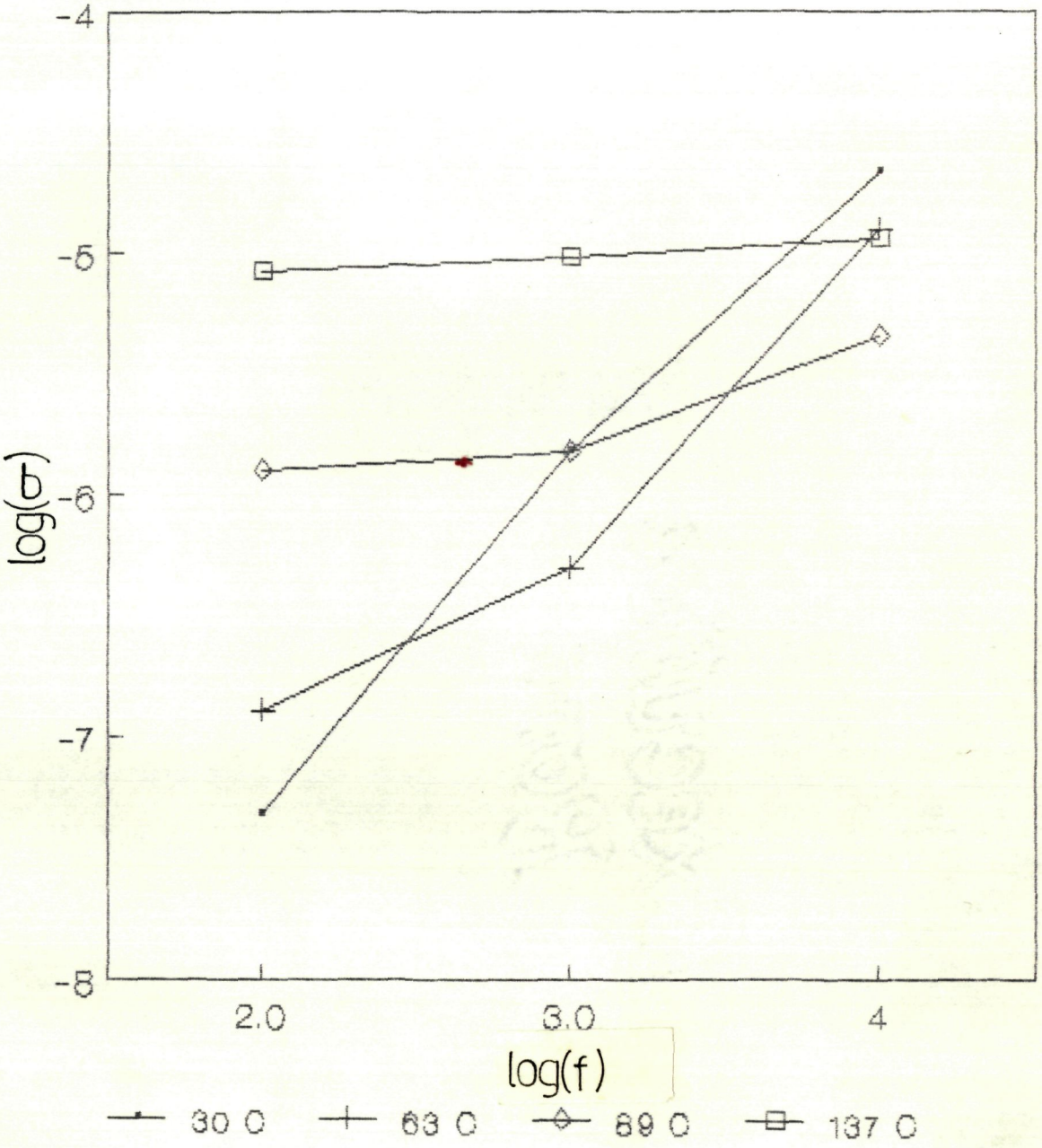

Fig. 2.3:Frequency dependence of the electrical conductivity of Cu_2HgI_4.

Compounds	Temperature region	Activation energy (KJ/mol)
Pure Ag_2HgI_4	A	27.35
	B	63.824
Pure Cu_2HgI_4	A	25.33
	B	91.91
50 mol% Ag_2HgI_4	A	31.91
	B	65.10
33 mol % Ag_2HgI_4	A	27.35
	B	59.57
68 mol % Ag_2HgI_4	A	65.65
	B	51.05

A, Pre-transition ; B, Post-transition

Table 2.1: Ionic conductivity activation energy values of Ag_2HgI_4 - Cu_2HgI_4 Solid solu tions

but in the case of 66 mol% Ag_2HgI_4 considerable decrease in Tc was observed. It undergoes a phase transition at 33°C much lower than that for parent compounds. The activation energy for ionic motion in the α-phase also shows a decrease in the 66 mol% Ag_2HgI_4, but the β-phase activation energy is slightly larger than that for the parent compounds. The electronic current carriers might be expected to be of less importance in the 66 mol% Ag_2HgI_4 with its highly mobile silver ions and, therefore, the β-phase activation energy is higher than that for the α-phase.

(b) Electrical conductivity studies of Cd^{2+} dopped 66 mol% Ag_2HgI_4

The temperature-dependent conductivity of 7 mol% Cd^{2+} doped 66 mol% Ag_2HgI_4 is presented in Fig.2.2 Cd^{2+} sample posses a higher conductivity than its undoped counterpart, the undoped sample conductivity is lower than that for the pure Ag_2HgI_4. Cd^{2+} was chosen as the dopant with the expectation that each would preferentially replace Cu^+ in the lattice because the Cd^{2+} and Cu^+ ions are having almost equal size [32] ($r_{Cd^{2+}}$ = 0.96 A°, r_{Cu^+} = 0.97A°). Since the Ag^+ is having a larger size than Cd^{2+}, r_{Ag^+} = 1.26A°, it can't be replaced by Cd^{2+}. The presence of Cd^{2+} on Cu^+ sites in the lattice would generate Cu^+ vacancies in accordance with the electroneutrality requirement. Vacancies

would permit greater facility of Cu^+ ion mobility and therefore enhance the ionic conductivity.

The activation energy values for ionic conductivity are tabulated in table 2.2. The constant activation energy value, 60 ± 3 kJ/ mol, for Ag_2HgI_4 and Cd^{2+} doped samples in the post-transition region suggest a common ionic conductivity mechanism. But the activation energy value for doped sample in the pre-transition region shows an increasing trend. However, the higher conductivity of the doped sample must be originate with the higher number of mobile charge carriers. That is, the kinetic mechanism remains same but the concentration factor, n, is increased by Cd^{2+} presence.

(c) Electrical conductivity studies of K^+ doped Ag_2HgI_4

Plots of log (σ T) versus 1/T for doped Ag_2HgI_4 are presented in Fig. 2.4. Similar plot is given for untreated Ag_2HgI_4 for comparison purposes. Ag_2HgI_4 doped with 5 mol% and 10 mol% K_2HgI_4, not shown in Fig. 2.4, exhibited the same σ-T behaviour as the 7 mol% doped sample. Similar σ-T behaviour for the 5 mol% 7 mol% and 10 ml%, K^+ in Ag_2HgI_4 suggests a saturation point of K^+ in the lattice. It can be observed that the K^+ doped sample undergoes a phase transition at about 60°C accompanied by a change of electrical conductivity phase transition temperature of the doped sample is intermediate between those of the parent

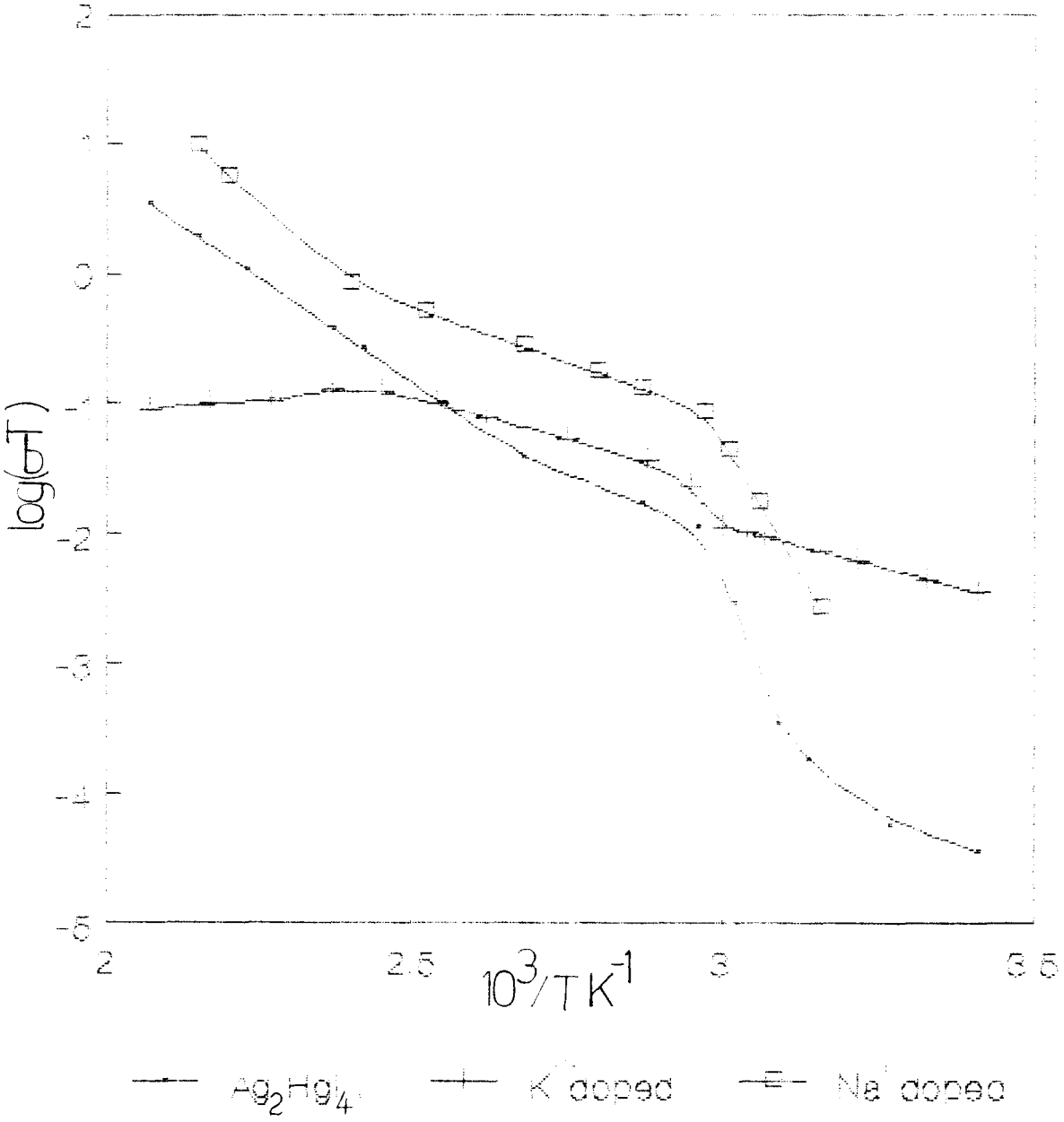

Fig.2.4:Temperature dependence of the electrical conductivity of K^+ and Na^+ doped Ag_2Hgl_4

compounds. It possesses a higher conductivity prior to the phase transition than the pure Ag_2HgI_4 and K_2HgI_4. The enhanced conductivity of doped sample is because of the lattice expansion due to the K^+ ion in the host lattice. K^+ ion is having slightly larger radius than that of Ag^+ ion (r_{K^+} = 1.33 A^o r_{Ag^+} = 1.26A^o). The introduction of this larger cation in the Ag_2HgI_4 lattice leads to the expansion of the lattice. The lattice expansion facilitates higher mobility of ions and hence, higher conductivity.

Another important feature observed in Fig. 2.4 is the erratic conductivity behaviour of the doped Ag_2HgI_4 in the post-transition region. After phase transition conductivity rises smoothly upto 135^oC, but above that it shows a decreasing trend. The drop in conductivity is due to the collapse of the iodide framework. The incorporation of K^+ ion causes the destruction of the sublattice. Such type of decrease in conductivity versus temperature has been reported for Na_2SO_4 [33] and K_2SO_4 [34].

The activation energy values for the ionic conductivity, Ea, in the pre-transition and post transition regions are tabulated in table 2.2. The constant activation energy values in the post transition region indicate a common conductivity mechanism.

Compounds	Temperature region	Activation energy (KJ/mol)
K^+ doped Ag_2HgI_4	A	22.97
	B	25.529
Na^+ doped Ag_2HgI_4	A	172.32
	B	31.912
Cd^{2+} doped 66% Ag_2HgI_4	A	153.11
	B	57.44
Pure Ag_2HgI_4	A	27.35
	B	63.824

A, Pre-transition ; B, Post-transition

Table 2.2: Ionic conductivity activation energy values of doped Ag_2HgI_4

(d) Electrical Conductivity studies of Na^+ doped Ag_2HgI_4

Since Ag_2HgI_4 exhibited high cationic conductivity in the high temperature phase [18], the prospect of higher cationic conductivity with smaller radius and lower mass Na^+, $r_{Na^+} = 0.96A^O$ versus $r_{Ag^+} = ,1.26A^O$, in the Ag_2HgI_4 structure prompted us to probe the nature of the solid - solid phase transition in Na^+ doped Ag_2HgI_4 Fig. 2.4 shows the temperature dependence of the electrical conductivity, , of 15% Na^+ doped Ag_2HgI_4 sample. The enhanced conductivity as pre dicted for Na^+ incorporated in Ag_2HgI_4 structure is observed. The activation energy values of pure and doped Ag_2HgI_4 in the post-transition region suggest, the major charge carrier in the doped sample to be Na^+ ions. The smaller size of Na^+ ions than Ag^+ ions would permit greater facility of Na^+ mobility and therefore enhance the ionic conductivity.

The σ T data reported in this study show that doped sample exhibit very high Na^+ ion conductivity in the high temperature phase analogous to the system of compounds $Na_3Zr_2Si_2PO_4$ referred to as NASICON [35]. The proposed model of highly mobil Na^+ ion in a fixed HgI_4^{2-} sublattice in $(Ag, Na)_2HgI_4$ compounds parallels the accepted model of highly mobile Ag^+ ion in a fixed network of I^- in AgI compounds [36].

Another important feature observed in Fig. 2.4 is the existence of different regions in the post-transition data. Above the phase transition conductivity data show clearly two different regions. The increase of the slope from region I to region II occurs at about 140^{o}C.

Usually the slope of the graph log (σT) versus 1/T gives directly the value of the activation energy, Ea. This is not true if Ea depends on temperature or if the conduction mechanism involves different reaction. Here in the region II, the activation energy is increasing with increasing temperature. The discontinuities in the evolution of the activation energy above the phase transition can be related to an extra enhancement of the I^- ion orientational disorder.

2.5 CONCLUSION

The studies on the phase transitions of Ag_2HgI_4 and Cu_2HgI_4 reveal that the 66 mol% Ag_2HgI_4 undergoes a phase transition at much lower temperature than the parent compounds. The incorporation of Cd^{2+} ion in 66 mol % Ag_2HgI_4 lattice shows a remarkable increase in conductivity due to the generation of vacancies in the host lattice. In K^+ doped Ag_2HgI_4 system, the destruction of the I^- sublattice take place when heated at above 135^{o}C. The lattice destruction

would effect a lower mobility of Ag^+ ion, thus a decrease in conductivity. The Na^+ doped samples exhibit very high Na^+ ion conductivity in the high temperature phase. The Na^+ ions are highly mobile due to the smaller size compared to Ag^+ ions. And above 140^oC the conductivity shows further increase due to the anion disorder.

The picture that emerges from the above discussions is that a closely related structure of a relatively open periodic I^- ion polyhedra exist in the high temperature phase. The open I^- framework facilitates the motion of the mobile cations contributing to the fast-ion or super ionic conductivity in these systems. The superionic conductivity can be affected by contraction or expansion of the sublattice, within the structural limits, effected by the guest cations of different ionic radii relative to the host cation and/ or by the presence of vacancies on cation lattice sites. This analyses further suggests that the presence of guest anion of different ionic radii and charge, eg WO_4^{2-} TeO_4^{2-}, Cd I^{2-}_4 etc. in the HgI_4^{2-} sublattice would effect similar or parallel behaviour.

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